

## Long-term and thermal instability of carbon/carbon composite

Witold Sokolowski, Kyle Brown, Tim O'Donnell and Stephen Jacobs \*

Jet Propulsion Laboratory  
California Institute of Technology  
Pasadena, CA 91109

### ABSTRACT

Very stringent dimensional stability requirements for metering rods of the NASA/Jet Propulsion Laboratory Cassini spacecraft NAC (Narrow Angle Camera) were the driving forces to select and conduct dimensional stability tests of several dimensionally stable materials. The carbon/carbon composite, among the other selected materials, was tested at the University of Arizona. Fabry-Perot laser-interferometric techniques were used to measure dimensional changes to accuracies in the 0.01 ppm range. Coefficient of thermal expansion (CTE), thermal hysteresis and temporal stability test results at 27.5°C and 38°C are reported here. The test results indicate that this carbon/carbon composite material, made from 2D fabric and pitch base fiber, appears to be the best among all tested nonmagnetic materials. CTE -1.5 ppm/°C are reported here along with temporal stability  $\leq 1$  ppm/year. However, relatively high thermal hysteresis within the temperature range of -48°C to +52°C may cause some concerns. Possible procedure to resolve this issue is also suggested here.

**Keywords:** carbon/carbon composites, thermal expansion, thermal hysteresis, temporal instability, Fabry-Perot resonator

### 1. INTRODUCTION

High performance requirements for the Imaging Science Subsystem (ISS)/Narrow Angle Camera (NAC) instrument on the NASA/JPL Cassini spacecraft imposed very stringent demands for dimensional stability of the metering rods in the athermalizing system. The metering rods are the primary component of the athermalizing system that allows the positions of a pair of optical elements to be controlled to compensate for bulk temperature changes. In order to meet the camera's optical requirements, the rods should meet rigorous requirements for very low thermal expansivity and temporal instability, possibly at a magnitude never required before. The metering rods must be made of a material with a coefficient of thermal expansion (CTE) of  $< 1$  ppm/°C and with combined temporal (long-term) stability and thermal hysteresis of  $< 1$  ppm/year.

It was a significant challenge to JPL to choose a material which could meet these dimensional stability requirements while still possessing other necessary attributes such as mechanical strength, machinability and space environment acceptability. In the selection process, Invar 36 material was chosen as the baseline material. Sokolowski et. al. described how HP (high purity) Invar 36 was fabricated and procured per JPL instructions, heat treated in order to improve dimensional stability even further and finally tested. As a result, JPL has succeeded in obtaining possibly the most dimensionally stable Invar 36 ever produced.

Due to a Invar 36 material magnetism issue and its possible interference with the ISS system and/or other nearby Cassini spacecraft instruments, other dimensionally stable, nonmagnetic candidate materials, such as silicon carbide, carbon/carbon composite and PI/EEK composite were selected and procured for test/evaluation as possible backup materials<sup>2</sup>. This paper describes why carbon/carbon composite material was chosen for this critical application, what carbon/carbon could be the best and which one was procured for testing because of availability. It also reports how procured carbon/carbon was manufactured and prepared for test. Finally, the paper describes the dimensional stability testing and discusses the test results, possibly the most accurate dimensional stability test ever done on carbon/carbon composite especially in temporal instability area.

\*Optical Sciences Center, University of Arizona

## II. DIMENSIONAL STABILITY OF CARBON/CARBON COMPOSITES

A carbon/carbon composite was chosen as a candidate material for metering rods for several reasons. First of all, it has good, tailorable thermal stability and light weight. Depending upon material architecture, type of fiber and matrix, and processes, the CTE of carbon/carbon in axial direction at near room temperature, has been reported<sup>2,3,4</sup> to vary from -2. to + 0.5 ppm/<sup>0</sup>C. The CTE of fibers themselves can differ from -1.5 to -0.5 ppm/<sup>0</sup>C in axial direction and approx. + 4 ppm/<sup>0</sup>C in transverse direction. On the other hand, the CTE of matrix could vary from -1.5 to + 4 ppm/<sup>0</sup>C. Therefore, if correctly tailored, the CTE of carbon/carbon could be near zero in required direction. Secondly, this material has the creep properties of a high temperature ceramic, which also made us believed in high resistance to dimensional changes with time but without applying any external stresses in isothermal, near room temperature environment. Finally, the modest difference in CTE between carbon matrix and carbon fiber could be accomplished by appropriate selection of the material architecture and type of fiber and matrix, in order to create low thermal hysteresis and good temporal stability.

There is a limited available data on thermal hysteresis and no data to our knowledge on temporal stability for the carbon/carbon composites. JPL has generated some amount of thermal cycling data under a carbon/carbon program funded by the Air Force Phillips Lab. The data is based on a sample of P-25 2K 8-Harness Sat in fabric which was densified by petroleum pitch and processed for low (near zero) CTE. The sample was cycled five times between -100<sup>0</sup>C and + 120<sup>0</sup>C in the materials lab's quartz beam dilatometer. The sample returned to the same end points after each cycle, but did show a hysteresis loop, which appears to diminish with increasing numbers of cycles.

The remainder of the data was produced by R. A. Meyer<sup>6</sup> of Aerospace Corporation. The samples used in this program were triaxially braided tubes, with approximately 25% axial fiber volume. The fibers used were Apollo 55 and P-75. Densification was by phenolic resin and by CVD. Thermal cycling was between -150<sup>0</sup>C and + 250<sup>0</sup>C, and thermal expansion behavior was measured by laser interferometer. The data shows CTE to be linear from -150<sup>0</sup>C to + 100<sup>0</sup>C, with a slight slope change at 0<sup>0</sup>C. Above +100<sup>0</sup>C the CTE gradually increases towards positive. This data also shows hysteresis above +100<sup>0</sup>C, but always returns to the original line below that temperature.

The unidirectional, low modulus PAN based fiber and low temperature heat treated/processed carbon/carbon was suggested to be chosen as a candidate material for metering rods. A low modulus unidirectional carbon/carbon composite would have, the least negative CTE. Thermal hysteresis would be reduced by use of a unidirectional composite because transverse matrix cracking structure would allow matrix to move with fiber without debonding. This is possible, because of the absence of the competing effects of positive transverse thermal expansion and negative axial thermal expansion of the carbon fibers. The matrix is also expected to orient preferentially parallel to the fibers in this material. The temporal stability was assumed to be excellent.

## III. CARBON/CARBON MATERIAL DESCRIPTION

A survey of various carbon/carbon manufacturers was conducted to determine if there were any samples available which were similar to the proposed material. The lead time for manufacturing carbon/carbon is such (approx. 12 weeks min.) that it was not possible to manufacture specific samples for the scheduled test, and therefore samples to be submitted for this test would have to be made from existing material made for other programs. The carbon/carbon composite made from 2D fabric and pitch based fiber P-25 was the only one among all carbon/carbon materials available at this time for testing. Several 1.27 cm thick plates of this material, found at the JPL Materials Lab, could be machined into samples suitable for the dimensional stability test. The 2D fabric and P-25 fiber carbon/carbon composite was not to be optimized material for the ISS metering rods. However, the temporal stability was expected to be very good.

The processing scheme of this material was as follows:

1. P-25/phenolic prepreg was laminated and cured as 1.27 cm thick panel
2. Panel was carbonized to 816<sup>0</sup>C
3. Panel was graphitized at 2206<sup>0</sup>C

4. Panel was reimpregnated with A240 pitch and carbonized to 816<sup>0</sup>C
5. Panel was graphitized at 2206<sup>0</sup>C
6. Panel was reimpregnated with A240 pitch and carbonized to 816<sup>0</sup>C

Later, the samples were machined using conventional abrasive machining into 0.95 cm square by 9.97 cm long rods. A 0.32 cm wide by 0.63 cm deep slot was cut down the center of one side (perpendicular to the plies) to allow for passage of the laser light through the sample. The slot was used because of the difficulty in boring a hole through the long axis of the sample, which is the usual configuration of samples used at the University of Arizona.

#### IV. TEST METHODS

The dimensional stability testing was conducted at Optical Sciences Center, University of Arizona. Two kinds of measurements were performed: thermal expansion (CTE/thermal hysteresis) and temporal instability. Both kind of measurements relied on the same laser-interferometric principle described previously in details<sup>7,8,9</sup>. The technique involved directing the beam from a tuneable HeNe laser sequentially through each Fabry-Perot sample-resonator (Fig.1), electronically locking the laser's frequency to the resonator's transmission peak and finally comparing the laser's frequency with that of a stable reference laser whose frequency was constant with time. When the sample length changed due to time or temperature changes, then the cavity resonant frequency changed by an amount  $\Delta$ . In this way, we could obtain an absolute measure of sample length through simple relation:

$$\Delta L/L = |\Delta \nu / \nu| \quad (1)$$

The experimental arrangement used for CTE/thermal hysteresis measurements is shown in Fig. 2. CTE/thermal hysteresis measurement was performed individually for one carbon/carbon sample in the temperature range of -48<sup>0</sup>C to +52<sup>0</sup>C, stopping every 25<sup>0</sup>C to record  $\Delta L/L$  and temperature. Plots were made of frequency shift vs. temperature, which were converted to  $\Delta L/L$  vs. temperature. The  $\Delta L/L$  and temperature data were recorded only after carbon/carbon sample length stabilized to  $\Delta L/L < .001$  ppm/hour.

The arrangement used for temporal stability measurements is shown in Fig. 3. Three carbon/carbon samples as well as other dimensionally stable materials samples were contained in a massive copper holder with the capacity of 37 samples. 2 samples were supplied by the University of Arizona: a copper sample was used for temperature stabilization and an optically contacted Homosil was used as a fused silica double check on the stability of reference laser. Temporal stability testing was conducted at 38<sup>0</sup>C for 80 days, after which the chamber temperature was dropped down to 27.5<sup>0</sup>C and the sample's length changes were monitored for another 43 days. Each weekday a measurement was made, sequentially, of initial chamber temperature, each sample's resonant frequency change and final chamber temperature. These resonant frequency changes were plotted vs. time and later converted to  $\Delta L/L$  vs. time.

#### V. EXPERIMENTAL TEST RESULTS

##### 1. CTE/thermal hysteresis

The CTE/thermal hysteresis testing was performed as planned within the temperature range of -48<sup>0</sup>C to +52<sup>0</sup>C. Only one thermal cycle was carried during this test. It was found out that carbon/carbon sample required very long length stabilization time compared to other materials tested, at each temperature stop. Since the carbon/carbon sample C/C4 took almost 2 weeks (over 10 working days) to run CTE/thermal hysteresis test, it was agreed not to measure the other two carbon/carbon samples and prolong the temporal stability test at ambient temperature (27.5<sup>0</sup>C).

The curves  $\Delta L/L$  vs. temperature are shown in Fig.4 and 5 and the test results are summarized in Table 1. The data illustrates low CTE of -1.50 ppm/<sup>0</sup>C to be fairly linear from -48<sup>0</sup>C to +52<sup>0</sup>C with a very slight slope change above temperature 0<sup>0</sup>C towards positive (-1.44 ppm/<sup>0</sup>C). These high negative CTE values do not meet requirements for metering rods of CTE  $\leq \pm 1$  ppm/<sup>0</sup>C.

TABLE 1

TAB 11{ 1  
CTE/Thermal Hysteresis Test Results

ID	$\frac{CTE}{+2^{\circ}C \text{ to } +27^{\circ}C}$ (ppm/ $^{\circ}C$ )	$\frac{CTE}{-48^{\circ}C \text{ to } +52^{\circ}C}$ (ppm/ $^{\circ}C$ )	$\frac{Hysteresis}{-48^{\circ}C \text{ to } +52C}$ (ppnl/cycle)
c/c 4	-1.44	-1.50	+ 5.70

The curves  $\Delta L/L$  vs. temperature also show in detail, how much this carbon/carbon sample failed to return to its original length upon return to its original temperature, which we refer to this as the thermal hysteresis. The expanded view near  $+27^{\circ}C$  (Fig. 5) demonstrates that a sample significantly expanded 5.7 ppm after 1 thermal cycle of  $+27^{\circ}C$  to  $+52^{\circ}C$  to  $-48^{\circ}C$  to  $+27^{\circ}C$  stopping every  $25^{\circ}C$  to record  $\Delta L/L$  vs. temperature. As mentioned before, the  $\Delta L/L$  and temperature data were recorded only after C/C sample length stabilized to  $\Delta L/L < .001$  ppm/hour. It took long times to achieve this stabilization at each temperature stop. in general, lower temperature, longer stabilization time: it took almost 43 hours for carbon/carbon sample to stabilize from  $-23^{\circ}C$  to  $-48^{\circ}C$  (Fig. 4)

## 2. Temporal stability

The temporal stability test was performed first for 60 days at a temperature of  $38^{\circ}C$  as planned. Later, in order to define a general trend of carbon/carbon behavior, it was decided to extend a test at this temperature for another 3 weeks and then drop the temperature down to ambient ( $27.5^{\circ}C$ ). This additional testing was done as an exchange for not doing very time-consuming CTE runs for the other 2 carbon/carbon samples. Due to cost consideration, all mirrors were held in place, by gravity, rather than by optical contacting.

All temporal stability data is summarized in Table 2. Temporal stability data for sample C/C4 at  $38^{\circ}C$  is shown in Fig 6. The length change rates represent the slopes of the linear portion of each curve  $\Delta L/L$  vs. days. U of A has fitted straight lines to the data. The least squares best fit analysis was not conducted because other uncertainties seemed far greater. In U of A judgement, all the nonlinear data and/or the discontinuities in data should be considered questionable with the best possible conclusion drawn from the linear segment. The most noticeable jumps and discontinuities in data are seen in the first 15 days of testing. The possible cause of these jumps and discontinuities could be due to test set-up: all Fabry- Perot mirror were held against the samples only by gravity, rather than by optical contacting. The U of A suspected these mirrors were vulnerable to jumps and settlements caused by vibration and perhaps dirt specks and/or electrostatic forces. Also thermal stabilization (temperature changes) of the testing system during the first days of testing could contribute to these jumps. The discontinuities on 64th day, lasted for following several days, were caused by temperature changes, intentionally performed to check the controlling system

TABLE 2  
Temporal Stability Test Results

ID	$\frac{38^{\circ}\text{C}}{80 \text{ Days}}$ (ppm/year)	$\frac{27.5^{\circ}\text{C}}{43 \text{ Days}}$ (ppm/year)
C/C1	0	+1
C/C2	+1	+1
C/C3	-1	0

The test results indicate very good temporal stability of tested carbon/carbon composite. At both temperatures  $38^{\circ}\text{C}$  and  $27.5^{\circ}\text{C}$ , temporal stability was  $\leq 1$  ppm/year for all tested carbon/carbon samples. In most cases, the samples were expanding with the rate of 1 ppm/year or did not change their lengths at all (0 ppm/year). One exception was a sample C/C3, which was shrinking 1 ppm/year at  $38^{\circ}\text{C}$ . All these results meet the temporal stability requirements for metering rods.

#### VI. DISCUSSION/CONCLUSIONS

The carbon/carbon composite made from 2D fabric and pitch based fiber P-25 was the only one among the carbon/carbon materials available at this time for testing. Therefore, it was not to be optimized material for the ISS metering rods and proposed unidirectional, low modulus based fiber carbon/carbon is expected to perform better especially in CTE and thermal hysteresis areas.

However, the test results indicate this 2D fabric and pitch based fiber carbon/carbon has very good temporal stability of  $\leq 1$  ppm/year at both temperatures  $38^{\circ}\text{C}$  and  $27.5^{\circ}\text{C}$ , which meet the temporal stability requirements for metering rods. Although its negative CTE of  $-1.5 \text{ ppm}/^{\circ}\text{C}$  does not meet the requirements of  $CTE \leq 1 \text{ ppm}/^{\circ}\text{C}$ , this carbon/carbon material appeared to be the best among all nonmetallic materials tested such as SiC, carbon fiber/PEEK composite when thermal expansion (CTE) is considered<sup>2</sup>.

On the other hand, high thermal hysteresis of  $+5.70 \text{ ppm/cycle}$  and long stabilization time should cause some concerns particularly where thermal cycling environment is anticipated. Whereas its high negative CTE can not be drastically improved by any heat treat/process, the thermal hysteresis could be possibly reduced by further thermal cycling. Unfortunately, only one thermal cycling between  $-48^{\circ}\text{C}$  and  $+52^{\circ}\text{C}$  was carried out during the test and we are unable to verify that further thermal cycling will reduce the thermal hysteresis.

The collected thermal cycling data on carbon/carbon and other composites suggests the beneficial effect of the thermal cycling on thermal hysteresis. As mentioned in this paper before, the thermal hysteresis data based on a sample of P-25 2K 8-Harness Satin fabric carbon/carbon indicated a thermal hysteresis loop, which appeared to diminish with increasing numbers of cycles. Other fiber reinforced composites such as boron reinforced aluminum showed length change during first thermal cycling but the amount of change decreased with each succeeding cycle, approaching an asymptote.<sup>10</sup> Similar effects had also been found in graphite/epoxy composites<sup>11</sup>. In general, the length changes during thermal cycling are associated with the residual stress relaxation and for composites, the internal micro-cracking could be additional mechanism for the dimensional changes. Therefore, possible benefits from thermal cycling before the assembly and service could be: residual stress relaxation, consumption of some dimensional changes, reduction of length change rate with time (temporal stability) and stabilization of carbon/carbon material.

## VII. ACKNOWLEDGEMENTS

The investigation described in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

The authors would like to acknowledge the support of Mr. Steve Gunter, Technical Task Manager and Mr. Marc Lane, Cognizant Engineer, Cassini ISS Mechanical Design Team. Also, the authors would like to thank Mr. Dan Bass, U of A, Dimensional Stability Laboratory for performing most of the measurements described here.

## VIII. REFERENCES

1. W. Sokolowski, S. Jacobs, M. Lane, T. O'Donnell and C Hsieh, "Dimensional Stability of High Purity Invar 36" SPIE Proc. Vol. 1993/15, 11-12 July, 1993, San Diego, CA.
2. W. Sokolowski, "Dimensional Stability Test Results of Candidate Materails for Metering Rods" JPL Internal Report, April 1993.
3. "Evaluation of Carbon/Carbon Composites for Advanced Turbine Engine Application, Preliminary Data Package, Mechanical/Thermal Properties of C-Cat Warp Aligned 2D CC" SORI-MER-84-17-5309-8 (Southern Research Institute), February 1985
4. R. W. Seibold, briefing "Carbon/Carbon Processing and Application" Presented to SAMPE, Foothill Chapter, 15 October, 1986
5. J. W. Finley, D. F. Raker, R. W. Lawley, J. L. McManus, "Spacecraft Application for Carbon/Carbon (SACC) Program" Report No. LMSC/F108936 (Lockheed Missile and Space Co, Sunnyvale, CA), 10 February, 1985
6. R. A. Meyer, "Microstructure and Its Possible Effects to CTE Behavior" Proc. of JANNAF RNTS Workshop on Carbon/Carbon Processing Science, April, 1988
7. J. B. Beerthold and S. F. Jacobs, "Ultraprecise Thermal Expansion Measurements of Several Low Expansion Materials" Appl. Optics, 15, 1976
8. "P. Baer, F. Kowalski, J. Hall, "Frequency Stabilization of a 0.633 Micron HeNe longitudinal Zeeman Laser" Appl. Optics 19, 3173, 1980
9. S. Jacobs, "Variable Invariables - Dimensional Instability with Time and Temperature" SPIE, C.R. July 1992, San Diego, CA
10. C. W. Marschal and R. E. Maringer, "Dimensional Stability, An Introduction, Pergamon Press, p. 187, New York, 1977
11. J. D. Forest, "Advanced Composite Missile and Space Design Data" General Dynamics Report No. GDCA-CHB72-001-6 to U.S. Air Force Materials Laboratory on Contract F33615-72-C-1388

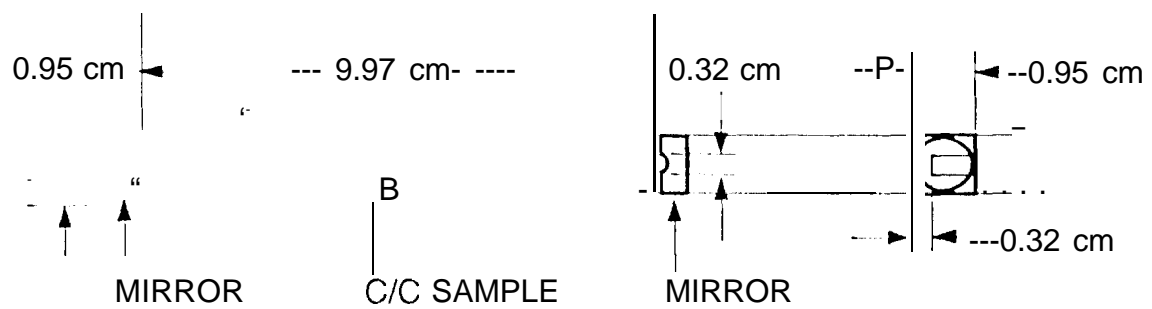


Figure 1. Test sample/etalon configuration.

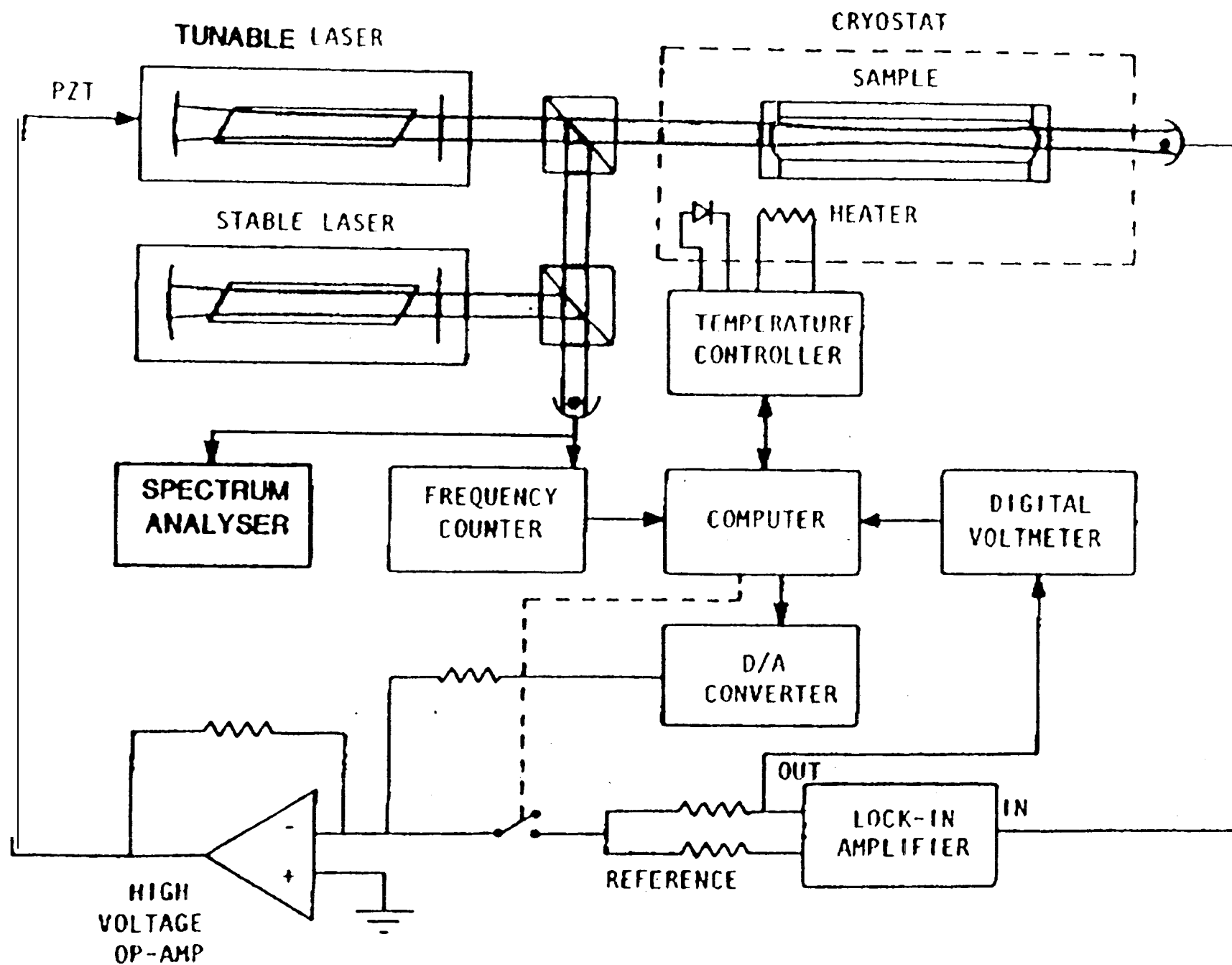


Fig. 2 Experimental Arrangement for Thermal Expansion Measurements.



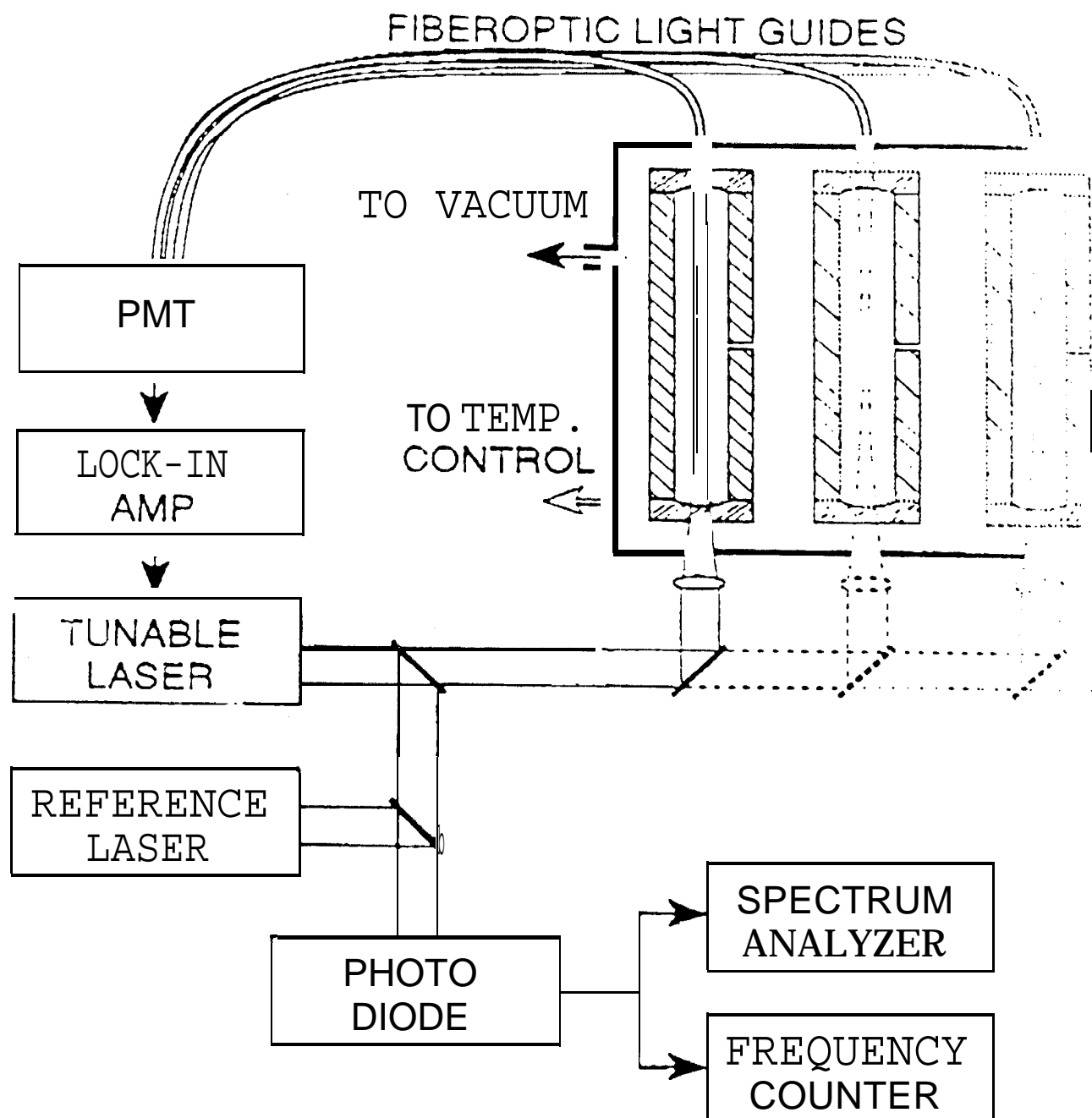


Figure 3. Arrangement used to study temporal stability.

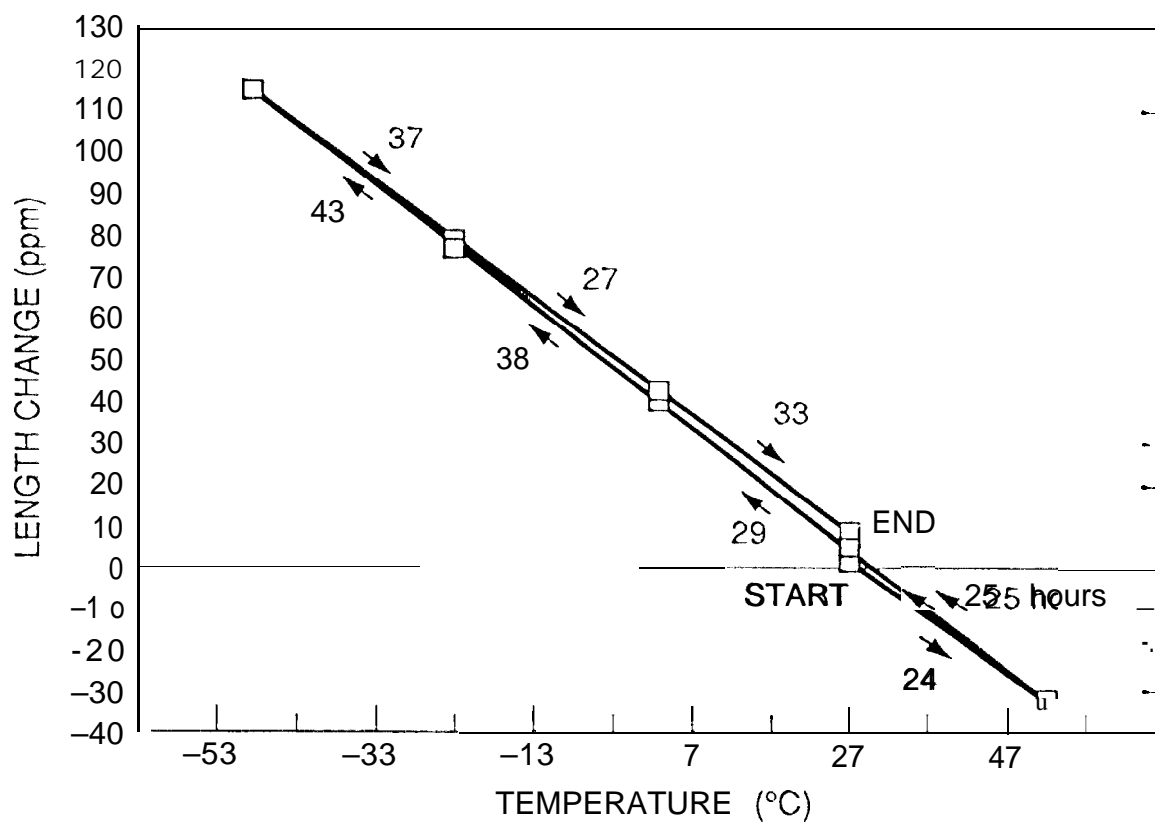


Figure 4. CTE/thermal hysteresis data for C/C4 sample; view of entire temperature range.

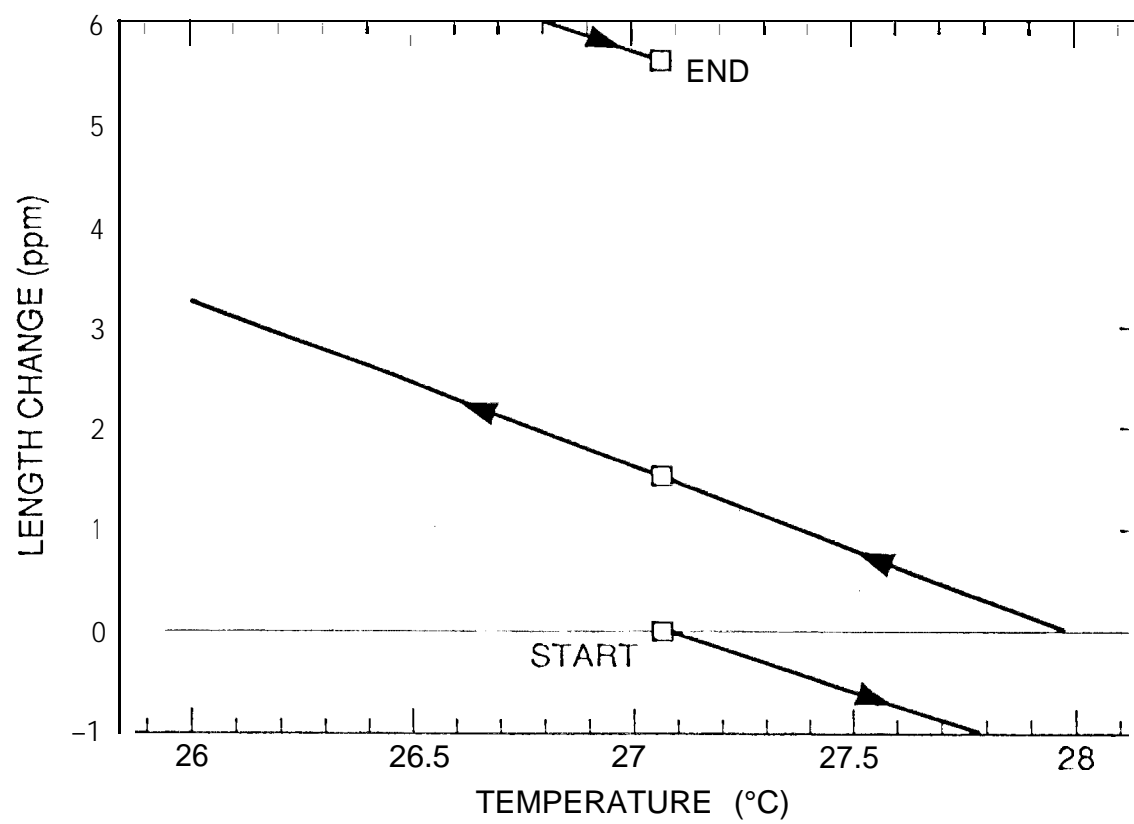


Figure 5. CTE/thermal hysteresis data for C/C4 sample; expanded view near 27°C.

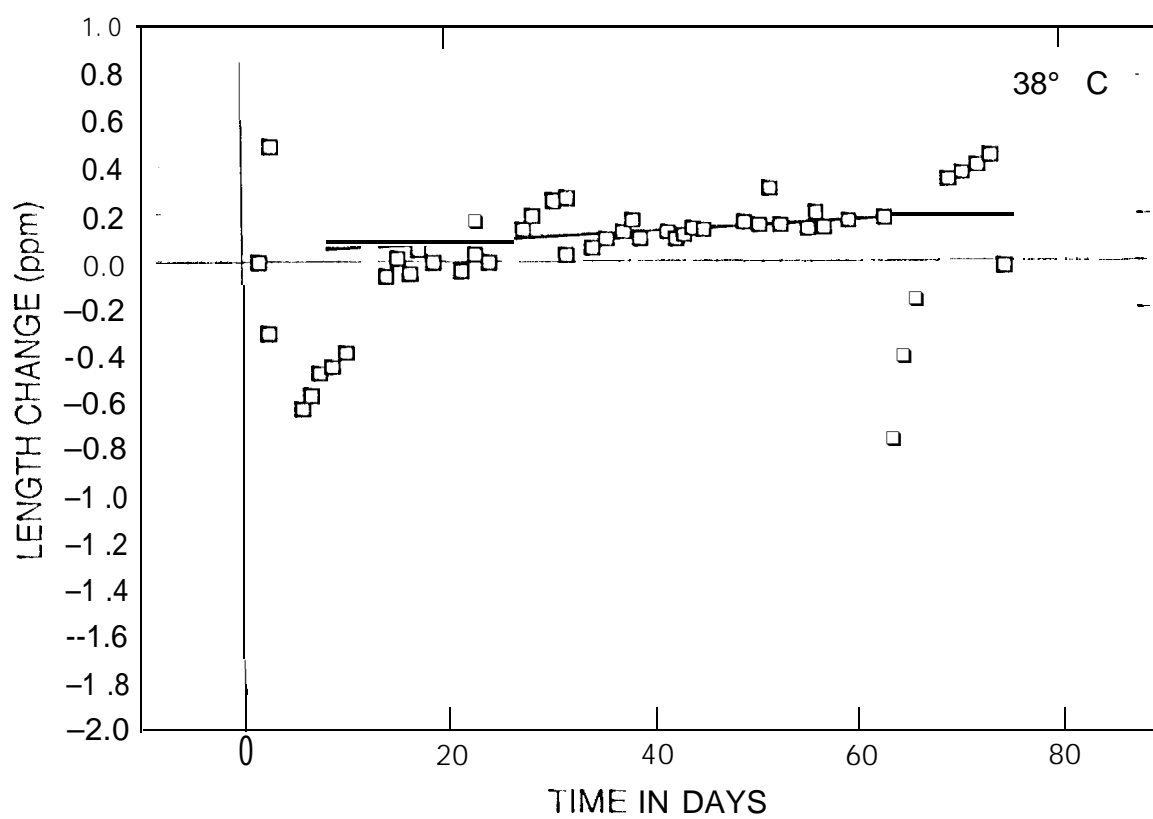


Figure 6. Temporal stability data for C/C2 sample at 38°C.